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## Infrared Dichroism and Orientation of Plasticizers in Stretched Polyvinylchloride Films

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Infrared dichroic measurements were made of stretched polyvinylchloride (PVC) films containing dioctyl phthalate and diethyl phthalate as plasticizer. It was concluded that dioctyl phthalate molecules added less than about 15 % were oriented keeping their relative orientation to PVC chain constant, and that those added more than about 15 % were dispersed freely in PVC medium. For the former case, the angles between PVC chain axis and three mutually orthogonal axes of benzene ring in phthalates were calculated from the orientation functions for the benzene absorption bands. The effect of alkyl chain length of phthalates on the orientation was discussed by comparing the results obtained for dioctyl phthalate and diethyl phthalate.

### INTRODUCTION

Many studies have been made of the nature and mechanism of plasticizing action. It is reported that the polar plasticizer such as phthalates, added to polyvinylchloride (PVC), make solvation with some active point of PVC<sup>1)</sup>. In order to confirm this, it is worthwhile to have informations about the orientation of plasticizer with respect to the PVC chain. Studies along this line, however, have been very limited in number.

On the other hand, in connection with the relative orientation between the polymer and the molecules added to the polymer, there are studies of the amorphous orientation by means of the visible dichroism of dyes incorporated into the polymer, and the polarization of fluorescence emitted from fluorescent molecules added or bonded to the polymer. These methods suffer from the disadvantage that the orientation of the added molecules with respect to the polymer chain segments is generally unknown, so that the accurate estimates of amorphous chain orientations have not yet been possible. The polarized infrared method has the advantage that one can measure the dichroism not only of the polymer but also of the added molecules, simultaneously.

In the present work, the infrared dichroism was measured for the stretched PVC films containing di-2-ethyl-hexyl phthalate (DOP) or diethyl phthalate (DEP). Besides ordinary polarized infrared spectra, use was made of the differential polarized spectra which were proposed by some of the present authors for precise measurement of low dichroism<sup>2)</sup>. From the results of dichroic measurements,

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the relative orientation with respect to PVC chain was argued. The effect of the alkyl chain length on the orientation is also discussed by comparison of the results obtained for DOP and DEP.

## EXPERIMENTAL

The PVC sample used is commercial *KANEVINYL S1001* from Kanegafuchi Chemical Industry Co., having the degree of polymerization of 1050 in average. It is said that the sample consists of nearly the same amount of syndiotactic and isotactic diads<sup>3)</sup>. DEP and DOP are of chemical grade. The mixture of PVC and DEP or DOP was dissolved into tetrahydrofuran to form 3-5% solution of PVC at room temperature, then casted so that the film thicknesses were between 8 and 40  $\mu$  depending on the intensity of the absorption band used, except for the very weak bands between 2000 and 1800  $\text{cm}^{-1}$  for which about 1000  $\mu$  films were used. The concentration of DEP or DOP in PVC was chosen to be various values less than 35 weight per cent. After full removal of the solvent at about 4°C in a refrigerator, the film obtained was stretched to various degrees of elongation in boiling water, and then quenched in cold water.

Infrared spectra were recorded by a Perkin-Elmer model 521 grating spectrophotometer. Two silver chloride polarizers were used for polarization measurements, being tilted 45° with respect to the entrance slit of the monochromator to eliminate the effect of polarization characteristics of the grating on the measurements. In the measurements of differential polarized spectra, the two polarizers and the sample were arranged with respect to the monochromator as described before<sup>2,4)</sup>. Such arrangement gives the quantity  $T$  shown by

$$T = I_s/I_r = 10^{-(A_{\parallel} - A_{\perp})} \quad (1)$$

on the recording paper, where  $I_s$  and  $I_r$  are the intensities of the sample beam and reference beam, respectively, transmitted through the sample, and  $A_{\parallel}$  and  $A_{\perp}$  are absorbances of the sample for the polarized radiations with the electric vectors parallel and perpendicular, respectively, to the stretching direction. Eq. (1) means that a parallel band ( $A_{\parallel} > A_{\perp}$ , and  $T < 1$ ) gives a downward peak in the differential polarized spectrum, whereas a perpendicular band ( $A_{\parallel} < A_{\perp}$ , and  $T > 1$ ) gives an upward peak.

Corrections were carried out for the imperfection of polarization in the transmitted beam of silver chloride polarizer used<sup>5)</sup>.

## RESULTS AND DISCUSSIONS

### 1. Ordinary polarized and differential polarized infrared spectra and band assignments

The ordinary polarized and differential polarized infrared spectra of the PVC film, containing 10 wt% DOP and stretched by 250% are shown in Figs. 1(a) and (b), respectively. Almost all the bands shown in Fig. 1 could not be used for evaluating the orientation of PVC and DOP because of overlap of the absorption

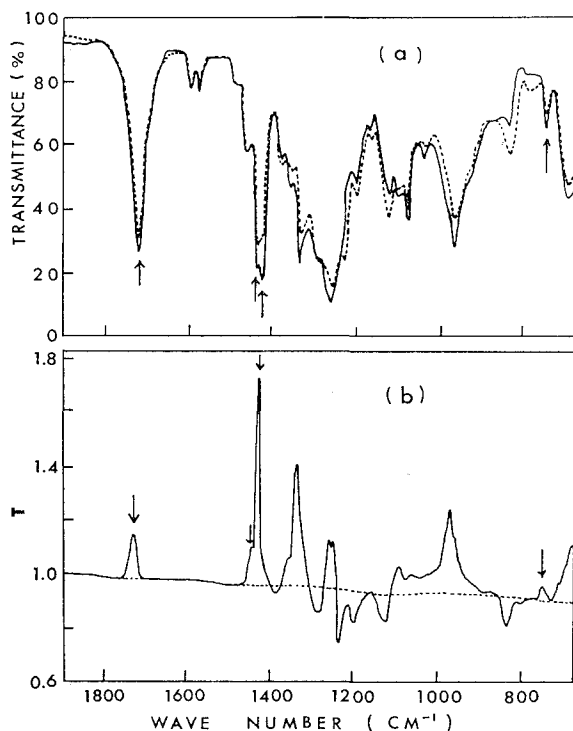


Fig. 1. (a) Polarized infrared spectra of a PVC film containing 10 % DOP and stretched by 250 %.

— electric vector perpendicular to elongation  
 ..... electric vector parallel to elongation

(b) Differential polarized infrared spectra of the same sample as (a).  
 The broken line is for no sample.

bands in both molecules. Only two bands of PVC and two bands of DOP shown by arrows in Fig. 1 were found to be free from the overlap and were used for the quantitative treatments. The situation was the same for the PVC film containing DEP.

Infrared absorption spectra of PVC having various conformations have been studied by many authors<sup>6-11</sup>). According to Germar *et al*<sup>11</sup>), the  $1426\text{ cm}^{-1}$  band was attributed to the bending mode of the  $\text{CH}_2$  group of the syndiotactic *TT* conformation, whereas the  $1435\text{ cm}^{-1}$  band to the same mode of the isotactic *TG* and syndiotactic *GG* conformations\*.

Pure DEP and DOP have the  $\text{C}=\text{O}$  stretching vibration band at  $1729$  and  $1730\text{ cm}^{-1}$ , respectively. When the molecules are dispersed into PVC medium, these bands shift to  $1725$  and  $1723\text{ cm}^{-1}$ , respectively. This frequency shift may be due to some interaction between carbonyl groups of phthalates and some active parts of PVC chain as was pointed out by Luther *et al*<sup>12</sup>).

\* The conformations of linear polymer molecules can be expressed by the consecutive arrangement of *T* (*trans* form) and *G* (*gausch* form) in a main chain. See S. Mizushima: "Structure of Molecules and Internal Rotation", p. 98, Academic Press, New York (1954).

# Infrared Dichroism of Plasticizers in Stretched PVC

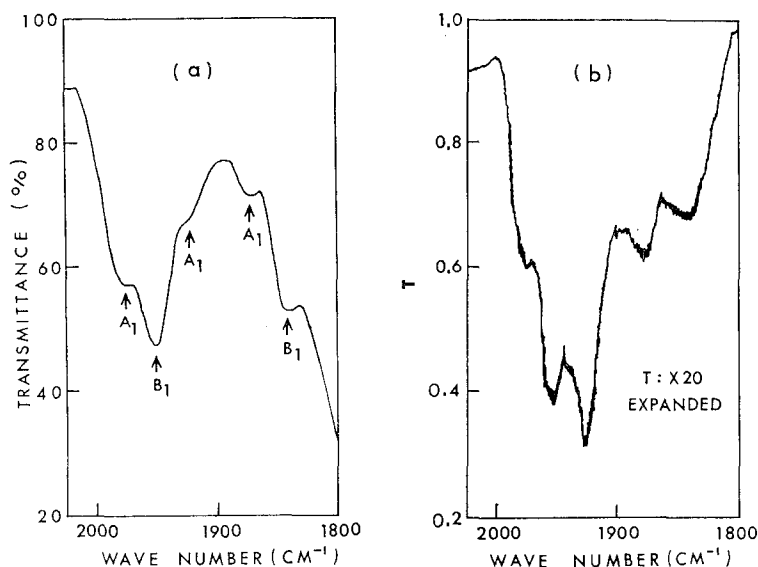
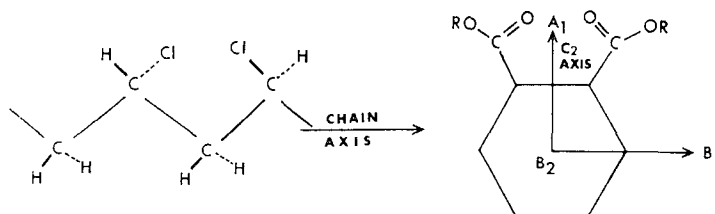


Fig. 2. Unpolarized (a) and differential polarized (b) infrared spectra of a PVC film containing 15 % DOP and stretched by 650 %.

Table 1. Assignments of bands used.

Wave number	Assignment	Symmetry species of $C_{2v}$	Transition moment
PVC 1426	CH <sub>2</sub> scissoring of syndiotactic <i>TT</i> unit		Perpendicular to chain axis
1435	CH <sub>2</sub> scissoring of isotactic <i>TG</i> unit and syndiotactic <i>GG</i> unit		See the text
<b>DEP DOP</b>			
745 743	CH out-of-plane deformation of benzene	( <i>B</i> <sub>2</sub> )	Perpendicular to benzene plane
1725 1723	C=O stretching		
1855 1840	Overtones and combinations of CH out-of-plane deformations (b, c & d) of benzene	b+c ( <i>B</i> <sub>1</sub> )	In-plane, perpendicular to C <sub>2</sub> axis
1886 1868		c+d ( <i>A</i> <sub>1</sub> )	In-plane, parallel to C <sub>2</sub> axis
1936 1918		2b ( <i>A</i> <sub>1</sub> )	In-plane, parallel to C <sub>2</sub> axis
1956 1946		b+d ( <i>B</i> <sub>1</sub> )	In-plane, perpendicular to C <sub>2</sub> axis
1984 1973		2d ( <i>A</i> <sub>1</sub> )	In-plane, parallel to C <sub>2</sub> axis



On the other hand, it is reasonable to consider that the CH out-of-plane deformation vibration at  $745\text{ cm}^{-1}$  (DEP) and  $743\text{ cm}^{-1}$  (DOP) belong to the  $B_2$  symmetry species having their transition moments perpendicular to the benzene ring, if the DEP and DOP molecules are assumed to have the symmetry of the point group  $C_{2v}$ . This assumption may not be strictly true for whole molecules, because the geometry of the substituents in these molecules is not known. But it may be virtually true as far as only the absorption bands of the benzene ring are discussed.

Figure 2(a) represents the unpolarized spectrum between  $2000$  and  $1800\text{ cm}^{-1}$  of a PVC film, containing 15% DOP and stretched by 650%. Five absorptions are observed in this region. As the intensity of these bands is much weaker than that of the bands shown in Fig. 1, thicker films were used in this case as compared with the previous case. Since dichroism of these bands is very small, it could hardly be detected by the ordinary polarized spectrum. Therefore the differential polarized spectrum was recorded as is shown in Fig. 2(b) with the ordinate scale expansion of twenty fold. According to Kakiuchi<sup>13)</sup> these bands can be assigned to the overtone or combination bands (the  $A_1$  or  $B_1$  species of the point group  $C_{2v}$ ) of the CH out-of-plane deformation vibrations of the substituted benzene ring.

The assignments of the bands shown in Figs. 1 and 2 are summarized in Table 1. Since the transition moments of the  $A_1$ ,  $B_1$  and  $B_2$  species bands are mutually orthogonal as shown in the figure in Table 1, the orientation of the benzene ring in phthalates could be completely evaluated using the  $A_1$ ,  $B_1$  and  $B_2$  species bands.

## 2. Evaluation of orientation : orientation function

In order to evaluate the orientation of PVC chain axis with respect to the stretching direction, a orientation function  $F$  defined by<sup>14,15)</sup>

$$F = f_a \cdot f_\theta \quad (2)$$

$$f_a = \frac{3\langle \cos^2 \alpha \rangle - 1}{2} \quad (3)$$

$$f_\theta = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \quad (4)$$

was used under the assumption of uniaxial orientation, where  $\alpha$  is the angle between the stretching direction and the PVC chain axis, and  $\theta$  between the PVC chain axis and the transition moment of the infrared absorption band.

For the  $1426\text{ cm}^{-1}$  band  $\theta$  can reasonably be assumed to have the value of  $\pi/2$ , so that the orientation function of this band is given by

$$F(1426) = -f_a/2 \quad (5)$$

Eq. (2) holds also for the bands of DOP and DEP, if  $\theta$  is replaced by  $\gamma$ ,  $\delta$  or  $\epsilon$ , which is the angle between the PVC chain axis and the transition moment of the  $A_1$ ,  $B_1$  or  $B_2$  species band, respectively, of DOP and DEP molecules, as shown in Fig. 3, that is,

$$F(A_1) = f_a \cdot f_\gamma \quad (6)$$

$$F(B_1) = f_a \cdot f_\delta \quad (7)$$

$$F(B_2) = f_d \cdot f_\varepsilon \quad (8)$$

$$f_\gamma + f_\delta + f_\varepsilon = 0 \quad (9)$$

The orientation function can be obtained from infrared dichroism of the band by

$$F = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp}) \quad (10)$$

$$A=(A_{\parallel}+2A_{\perp})/3 \quad (11)$$
$$F = (A_{\parallel} - A_{\perp})/3A' \quad (12)$$

### 3. Variations in the orientation function with elongation

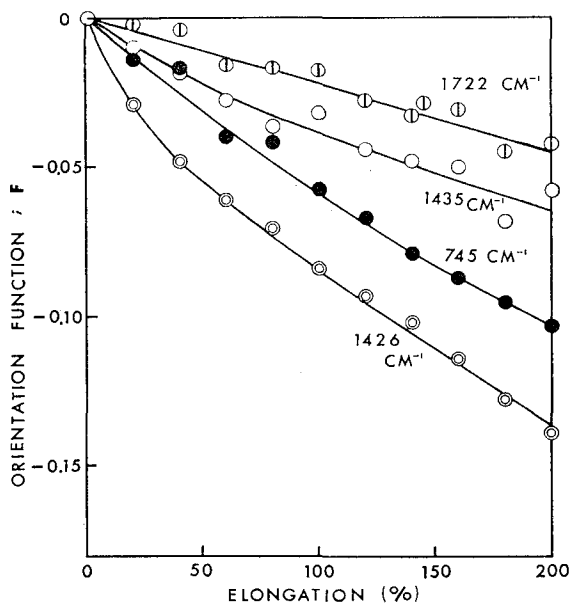


Fig. 4. Variations in orientation functions with elongation of PVC films containing 6.3% DEP.

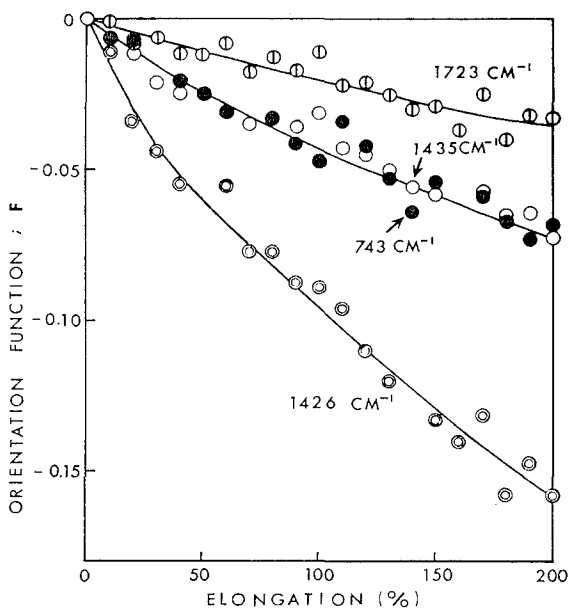


Fig. 5. Variations in orientation functions with elongation of PVC films containing 10% DOP.

Figs. 4 and 5 show variations in the orientation functions with elongation of PVC films containing 6.3 wt. % DEP and 10 wt. % DOP (equivalent in molar per cent), respectively. The  $F$  values decreases smoothly with elongation. The ratios of  $F$  values of DEP and DOP to those of PVC are constant throughout the whole degree of elongation examined. This fact suggests that the plasticizer



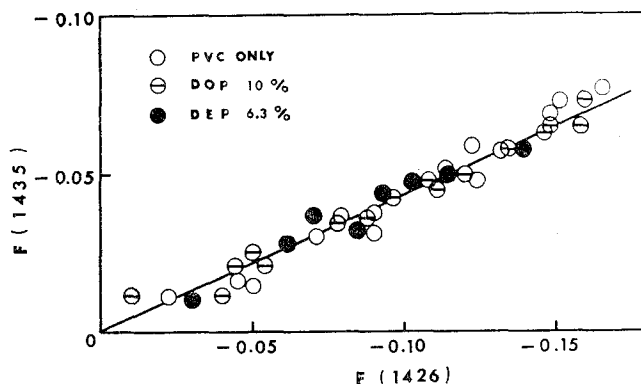


Fig. 6. Correlation between  $F(1435)$  and  $F(1426)$  of PVC.

molecules follow closely the orientation of PVC chains when PVC films are stretched.

The absolute value of  $F(1426)$  is always larger than that of  $F(1435)$  as is seen in Figs. 4 and 5. In Fig. 6 the values of  $F(1435)$  at various degrees of elongation are plotted against the corresponding values of  $F(1426)$ , including the case of pure PVC films. All points lie on a straight line. As is described before, the  $1426\text{ cm}^{-1}$  band is assigned to the  $\text{CH}_2$  bending mode of the syndiotactic  $TT$  conformation (trans zigzag carbon skeleton) with its transition moment perpendicular to the chain axis. On the other hand, the  $1435\text{ cm}^{-1}$  band is mainly ascribed to the  $\text{CH}_2$  bending mode of the isotactic  $TG$  conformations and partly to that of the syndiotactic  $GG$  conformations (the bent part of the zigzag carbon chain). The sequence of isotactic  $TG$  units forms three-fold helix, and the transition moment of  $\text{CH}_2$  bending vibration band ( $1435\text{ cm}^{-1}$ ) of this conformation is not perpendicular to the helix axis. It is therefore expected that the absolute value of the orientation function for the  $1435\text{ cm}^{-1}$  band is smaller than that for the  $1426\text{ cm}^{-1}$  band, even if the orientation of the helix axis of the isotactic  $TG$  conformation is the same as that of the chain axis of the syndiotactic  $TT$  conformation. Assuming that this is the case and neglecting the contribution of syndiotactic  $GG$  units and isolated  $TG$  units to  $1435\text{ cm}^{-1}$  band, the transition moment of the isotactic  $TG$  units is determined to form the angle of about  $64^\circ$  with the helix axis from the slope of the line in Fig. 6. This means that the  $\text{C}-\text{C}-\text{C}$  angles of the three-fold helix is about  $128^\circ$  which is somewhat larger than tetrahedral angle  $109^\circ 28'$ .

Hereafter,  $F(1426)$  will be used to evaluate the orientation of PVC chains under the assumption that the orientation of the helix axis of the isotactic  $TG$  units are nearly the same as that of the chain axis of the syndiotactic  $TT$  units.

#### 4. The relative orientation between phthalates and PVC

In Fig. 7, the values of  $F(745)$  of DEP and  $F(743)$  of DOP are plotted against those of  $F(1426)$ , showing the linear relationships. This fact suggests that the values of  $f_e$  is constant independent of the degree of elongation. Putting this slope equal to the ratio of Eqs. (8) to (5), the values of  $f_e$ ,  $\langle \cos^2 \epsilon \rangle$  and  $\epsilon_M$  can be obtained as is shown in Table 2. The difference in  $\langle \cos^2 \epsilon \rangle$  or  $\epsilon_M$  can be

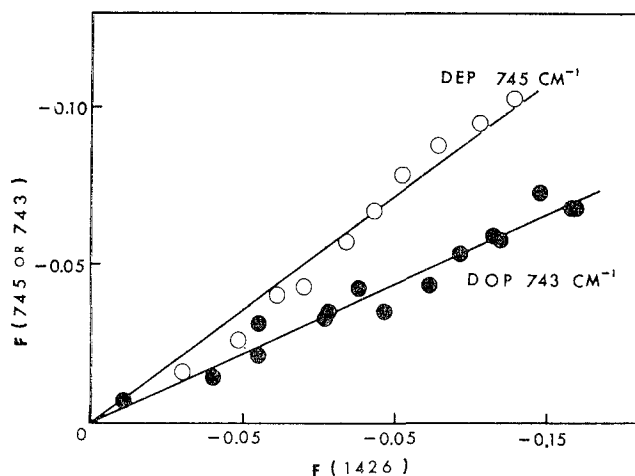


Fig. 7. Correlation between  $F(745)$  of DEP or  $F(743)$  of DOP and  $F(1426)$  of PVC.

Table 2.

	DEP	DOP
$f_\varepsilon$	-0.36	-0.22
$\langle \cos^2 \varepsilon \rangle$	0.093	0.187
$\varepsilon_M$	71°	64°
$F(A_1)^*$	0.094	0.065
$F(B_1)^{**}$	0.043	0.023
$f_\gamma$	0.24 <sup>8</sup>	0.16 <sup>2</sup>
$\langle \cos^2 \gamma \rangle$	0.49 <sup>8</sup>	0.44 <sup>1</sup>
$\gamma_M$	45°	48°
$f_\delta$	0.11 <sup>3</sup>	0.058
$\langle \cos^2 \delta \rangle$	0.40 <sup>8</sup>	0.37 <sup>2</sup>
$\delta_M$	50°	52°
$\beta_M$	39°	40°

\* The average value of three  $F(A_1)$ .

\*\* The average value of two  $F(B_1)$ .

seen between DEP and DOP. Larger value of  $\varepsilon_M$  in DEP shows that the benzene plane of DEP orients more parallel to the PVC chain than that of DOP does. The ethyl-hexyl groups in DOP is bulkier than the ethyl groups in DEP, and this bulkiness of the ethyl-hexyl groups seems to reduce the parallelism of the benzene plane to the PVC chains.

The next step is to obtain the values of  $f_\gamma$  and  $f_\delta$  by the use of the results shown in Figs. 2(a) and 2(b). As the dichroism of these bands is small, Eq. (12) instead of Eq. (10) was used to get the orientation function  $F$ . This film was so thick that the dichroism of the 1426 cm<sup>-1</sup> band could not be measured. Therefore,  $f_\gamma$  and  $f_\delta$  could not be obtained from Eqs. (5), (6) and (7). The values of  $f_\gamma$  and  $f_\delta$  were obtained from the ratio of  $F(A_1)$  to  $F(B_1)$ , i.e.,  $f_\gamma/f_\delta$  and Eq. (9). In this case,  $f_\varepsilon$  in Eq. (9) was assumed to be the same as that in the elongation less than 200%. The results are listed in Table 2.

The differences in  $\gamma_M$  and  $\delta_M$  between DEP and DOP are not so large. This fact and the above-mentioned frequency shift for the C=O stretching vibration seem to mean that the ester groups of substituents in phthalates play the important part in the stable orientation of phthalates to PVC chain.

The angle  $\beta_M$  between the  $A_1$  direction and the projection of the PVC chain axis on the benzene plane can be obtained from already-known  $\gamma_M$  and  $\varepsilon_M$ , using the next relationships,

$$\cos \gamma_M = \cos\left(\frac{\pi}{2} - \varepsilon_M\right) \cdot \cos \beta_M \quad (13)$$

The result is listed in Table 2. Little difference in  $\beta_M$  between DEP and DOP also suggests the role of the ester groups in the phthalate orientation described above.

##### 5. Variations in orientation functions with DOP content

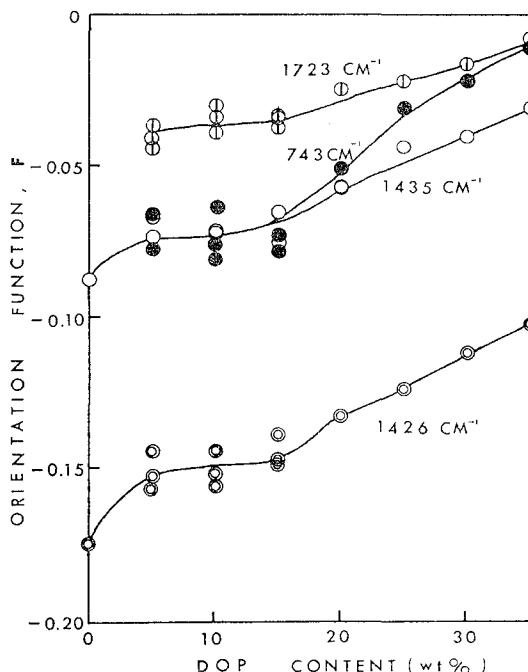


Fig. 8. Variations in orientation functions with DOP content in PVC films stretched by 200%.

Figure 8 shows variations in orientation functions with DOP content in PVC films stretched by 200 %. As the DOP content increases, the values of orientation functions of all the PVC and DOP bands examined increase slowly till about 15 % content, and rapidly thereafter. At the same time the coincidence of  $F(1435)$  and  $F(743)$  observed at less than about 15 % content disappears at higher content, where  $F(743)$  increases more rapidly than  $F(1435)$  does. This seems to show that the limit of so-called "solvation" of DOP to PVC is about 15 % content and that DOP molecules added more than about 15 % content are dispersed comparatively freely in the PVC medium. The same results have been obtained by other methods such as broad line NMR<sup>17)</sup>, and dielectric<sup>17)</sup> and mechanical losses<sup>18)</sup>.

The increase of the value of  $F(1435)$  or  $F(1426)$  at more than about 15 % content seems to be due to the release of entanglements between PVC chains themselves by the presence of the free DOP molecules. The release of entanglements may increase the freedom of PVC chains, so that the degree of orientation may be lowered.

## 6. Variation in the conformation of PVC with elongation

Figure 9 shows the variation in the ratio  $A(1426)/A(1435)$  with elongation. It is seen that the relative intensity of  $1426\text{ cm}^{-1}$  band to that of  $1435\text{ cm}^{-1}$  band increases slightly with elongation regardless of the concentration of DOP. This fact suggests the partial interconversion from syndiotactic *GG* conformation into *TT* conformation by stretching, that is, the interconversion from bent syndiotactic chain into straight zigzag chain. In this process, the degree of crystallinity may be

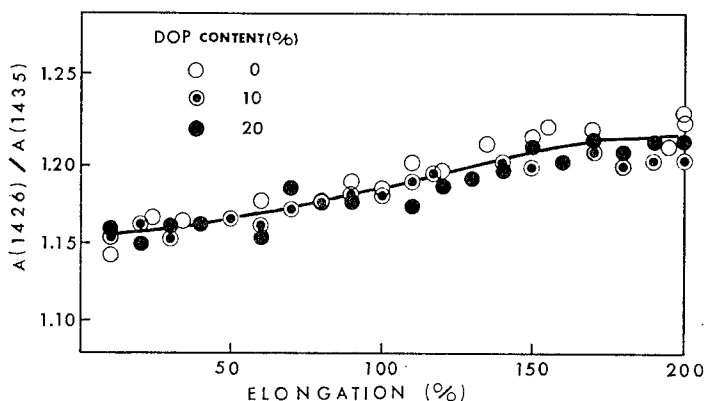


Fig. 9. Variation in the ratio of  $A(1426)/A(1435)$  with elongation of PVC films.

increased slightly.

#### ACKNOWLEDGEMENT

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